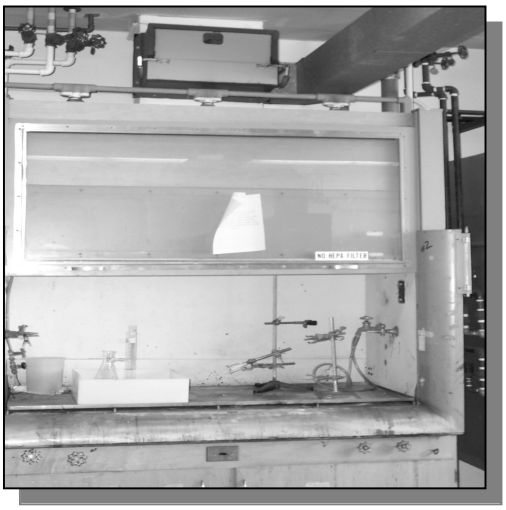
Perchloric Acid Sampling and Analysis Procedure

Content



1.0 Purpose/Scope

This document describes a field procedure for taking and analyzing wipe samples of surfaces potentially contaminated with perchlorates and perchloric acid. It is based on methodology described *in Perchloric Acid Contaminated Hood Decontamination Procedure Manual* (1993), prepared by ORNL. The goal of the procedure is to provide a uniform method to collect representative samples of surface contamination and to provide a standardized, accurate method to analysis the concentration. Using this method will ensure repeatability between various sampling personnel and surface configurations.

Scope: This field procedure describes elements necessary for sampling using practices developed by organizations based on lessons learned experience. This procedure should be viewed as a best management practice. Regulatory limits for surface contamination with perchlorates do not exist, but this method allows quantification of surface levels for comparison with known safe levels from industry experience.

This program is implemented through the SHSD Industrial Hygiene Group Leader who may delegate authority to administer this program. Members of the SHSD Industrial Hygiene Group, the Radiation Control Division Facility Support Group, and Plant Engineering are potentially qualified to perform certain tasks in this program based. Personnel who have demonstrated competency in performing a certain role, in accordance with the Policy Section of this procedure, will be qualified to serve that role by the Group Leader or Program Administrator.

2.0 Responsibilities

2.1 Chain of Custody procedures: The collector of the sample is responsible for the integrity of the sample until the sample has been properly transferred to the IH Group laboratory using the SHSD established *Chain of Custody* procedures. It is permissible to use this procedure to collect samples that will be analyzed by a laboratory not associated with the SHSD IH Group.

2.2 Hazard Analysis of the Sampling Task: It is the responsibility of the person using this method and his/her supervisor to ensure that the appropriate personal protective equipment is worn while performing this procedure. In addition, the person performing this procedure and his/her supervisor are responsible to ensure that all required training and qualification for hazards that may be present in areas where this procedure will be used (such as respiratory protection or radiation contamination) have been met. The person performing this procedure and his/her line supervisor are responsible to comply with all work planning and work permit system requirements.

3.0 Definitions

3.1 **Qualified Sampler***:* A person who has demonstrated competency, in accordance with Section 4, to perform this field procedure.

3.2 **Qualified Analyzer**: A person who has demonstrated competency, in accordance with Section 4, to perform this analysis procedure.

4.0 Prerequisites

4.1 **Qualification Criteria:** Only persons who have demonstrated competency in performing this test, to the satisfaction of the IH Group Leader or their designee will be qualified to perform this test. The qualification criteria to perform this procedure are:

4.1.1 Knowledge of industrial hygiene practice (awareness level).

4.1.2 Specific knowledge of this procedure.

4.1.3 Demonstrated competency in performing this test to the satisfaction of the IH Group Leader or Program Administrator via:

- Visual observation of the sample wiping technique and/or analysis procedure.
- Ability to answer questions on the sampling and analysis procedure and chain of custody of the sample during sampling and transportation.

- Knowledge of the appropriate personal protective equipment for the hazards of this particular type of sampling.

4.2 **Qualification Frequency & Record-keeping:** The SHSD IH Group Leader, Program Administrator, or their designee will qualify SHSD IHG personnel to use this procedure.

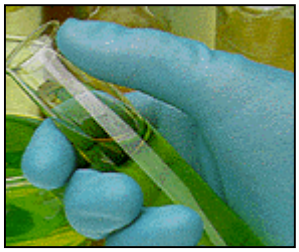
4.2.1 Personnel shall be re-qualified at a frequency not to exceed three years, provided there is no break in the work assignment that utilizes this procedure.

4.2.2 If a person has not performed a Perchloric Acid sampling and sample analysis for a period of over 1-year from the date of last qualification, demonstration of competency to perform this procedure to the satisfaction of the person's supervision will be required before sampling commences. The supervisor may ask for the assistance of the Program Administrator to assist in re-qualification, at the discretion of the supervisor.

5.0 Precautions

5.1 **Personal Protective Equipment**:

5.1.1 **Sampling:** Appropriate personal protective equipment to protect the person collecting the sample must be used when implementing this procedure. At a minimum, disposable gloves must be used when contacting the surface material and handling exposed sampling media. The gloves must have sufficient impermeability to the surface contaminant and solvent used on the collection media to allow safe handling. Recommended gloves are disposable Nitrile, Natural Latex Rubber, or PVC. During sampling, where the potential for contamination of the body can occur, the use of disposable clothing to cover the areas of contact is required.



5.1.2 **Analysis:** Disposable gloves must be used when mixing the 70% Perchloric acid and should be used when handling the glassware and pipettes containing diluted perchlorates. Recommended gloves are disposable Nitrile, Natural Latex Rubber, or PVC.

5.2 **Radiation Contamination:** It is possible that some surfaces to be tested may have radiation contamination as well as the chemical contamination. In these cases, personal protective equipment and administrative controls must be implemented for the radiation

contaminant hazard in addition to the chemical hazard. In addition, the collected sample must be analyzed for the radiation hazard before it can be submitted to the IH Group for analysis of metal or chemical concentration. At no time will the IH Group accept a sample with radiation contamination above permissible limits for the general public.

5.3 **Work Planning:** All requirements of work permits and work planning system reviews must be met in performing this procedure.

5.4 **Perchlorate Hazard:** Crystals of perchlorates, when dry, pose an explosion hazard when disturbed. The bottle containing the 70% solution of Perchloric Acid should be kept moist at all times to prevent the formation of perchlorates at the interface of the bottle and cap. To achieve this, the acid bottle is stored within a second bottle containing a moist paper towel.

6.0 Procedure

6.1 Equipment

Sampling

6.1.1 4x4 inch cotton gauze or equivalent
6.1.2 Rod or extension device
6.1.3 Deionized or distilled water
6.1.4 Sample containers
6.1.5 Gloves

Analysis

6.1.6 Ion selective electrode testing kit
6.1.7 Water sprayer
6.1.8 Suction pump or equivalent equipment
6.1.9 Tygon tubing
6.1.10 Flasks
6.1.11 2M Ammonium Sulfate solution (See 6.3 for preparation)
6.1.12 Ion Buffer (See 6.3 for preparation)
6.1.13 2000 ppm Perchlorate Stock (See 6.3.4 for preparation)
6.1.14 Orion Model 290A pH/mV meter
6.1.15 Orion dual probes:
- Yellow reference probe
- Black Perchlorate probe

6.2 Perchloric Acid/Perchlorates Field Sample Collection

6.2.1 Sampling a hood and exhaust stack

6.2.1.1 Secure a piece of gauze to a wooden rod or extension device. A rubber bad typically secures the gauzes well.
6.2.1.2 Moisten the gauze with the deionized or distilled water.
6.2.1.3 Wipe/rub the edge of the upper baffle near the duct and around the mouth of the duct.
6.2.1.4 Wipe the inside of the duct walls, if possible.
6.2.1.5 Using gloves, remove the gauze and place into a labeled sample container.
6.2.1.6 Add **25mL** of deionized or distilled water.
6.2.1.7 Shake the vial for at least one minute.
6.2.1.8 Proceed to section 6.3 for analysis procedure.

6.2.2 Sampling a fan housing

6.2.2.1 Spray about 1 liter of deionized or distilled water into the fan housing.
6.2.2.2 Direct the spray toward the fan while someone slowly turns the fan shaft.
6.2.2.3 Allow the water to accumulate at the bottom of the fan housing.
6.2.2.4 Feed Tygon tubing into the fan housing until the tube reaches the wash water.
6.2.2.5 Turn on a suction pump to collect a sufficient sample volume (50-800mL).
6.2.2.6 Proceed to section 6.3 for analysis procedure.

6.2.3 **Label the container used to collect the sample**. The label should include the following:

6.2.3.1 Date
6.2.3.2 Building and room identification
6.2.3.3 Source identification
6.2.3.4 Location in the exhaust ventilation system where sampled (i.e., hood, fan, stack, etc.)
6.2.3.5 Suspected sample contents—contaminant
6.2.3.6 Specific location of each sample
6.2.3.7 Surface Area sampled
6.2.3.8 Samplers name

6.3 Perchloric Acid Laboratory Analysis

6.3.1 Ammonium Sulfate solution preparation

6.3.1.1 Tare a piece of weighing paper on the balance.
6.3.1.2 Weight **26.43** +/- 0.5 **grams** of Ammonium Sulfate on the balance.
6.3.1.3 Dissolve the 26.43g of Ammonium Sulfate in approximately 50mL deionized or distilled water in a 100 ml beaker.
6.3.1.4 Transfer the solution to a 100mL volumetric flask.
6.3.1.5 Rinse beaker with deionized or distilled water; transfer the rinses to the volumetric flask.
6.3.1.6 Repeat until beaker is clean.
6.3.1.7 Bring flask up to the **100mL** mark with de-ionized or distilled water.
6.3.1.8 Stopper and invert to mix.
6.3.1.9 Label flask as ***"2M Ammonium Sulfate"*** with the current date.

6.3.2 Ion Buffer solution preparation

6.3.2.1 Pipette 2mL of the *2M Ammonium Sulfate Solution* into a 100mL volumetric flask and fill to the mark with deionized or distilled water.
6.3.2.2 Label the flask "***Ion Buffer solution***".

6.3.3 Instrument set-up

6.3.3.1 **Battery Check:** On the Orion Model 290A pH/mV meter, check the battery status by turning the meter "on" (press the **"Power"** button). Replace the 9V-battery if no display occurs.
6.3.3.2 **Reference Electrode:** Flush the yellow, double junction reference electrode with distilled water. (Note: Refill with the ion buffer before each set of measurements.)

- Fill the inner chamber with the manufacturer supplied "***Double Junction Reference Electrode Inner Filling Solution",*** Orion Part Number 900002.
- Fill the outer portion with the ***Ion Buffer Solution*** prepared in Step 6.3.2.

6.3.3.3 **Specific Ion (Perchlorate) Electrode:** Remove the rubber end-cap from the black 93 Series

Electrode Body (if new or dry stored) or remove the probe from its long-term storage distilled water bath.

6.3.3.4 **Establishing a Baseline Meter Reading:**

6.3.3.4.1 Place both probes approximately 1" to 2" into deionized or distilled water in a beaker for 5 to 10 minutes.

6.3.3.4.2 Place both probes into a 100 ml beaker containing the ion buffer solution to 1" to 2" depth. Insert a stirring bar and place the beaker and probes on a stirring plate. Spin the bar.

6.3.3.4.3 Turn the meter "on". Use the **"mode"** button to select the **"mV"** setting. If the reading does not stabilize and have a reading **>280mV**, the Perchlorate probe is "bad" and should be replaced. (See pg. 16 of the Orion Instruction Manual for Perchlorate electrode 93-81.)

6.3.3.4.4 Record the meter reading of the perchlorates in the *Ion Buffer Solution* on the *Analysis form*.

6.3.3.4.5 Rinse the probes with distilled water between solutions.

6.3.3.4.6 Place the probes into distilled water and record the mV reading on the *Analysis form*.

6.3.4 Perchlorate Stock solution preparation

6.3.4.1 Pipette **0.173mL** of 70% Perchloric acid into a 100mL volumetric flask.

6.3.4.2 Add distilled or deionized water to the **100mL** mark, cap the flask, and invert to mix.

6.3.4.3 Label as "*2000ppm Perchlorate Stock*" and mark the date on the flask.

6.3.5 Calibration Standards preparation

6.3.5.1 Calibration Solution 1: Using a volumetric pipette, pipette **0.5mL** of the *2000ppm-perchlorate stock* into a 50mL volumetric flask.. Add **2mL** of 2M Ammonium Sulfate and fill to the mark with deionized or distilled water. Label as "*20ppm-perchlorate calibration standard.*"

6.3.5.2 Calibration Solution 2: Using a volumetric pipette, pipette **5.0mL** of the 2000ppm-perchlorate stock into a 50mL volumetric flask. Add **2mL** of 2M Ammonium Sulfate and fill to the mark with deionized or distilled water. Label as "*200ppm-perchlorate calibration standard*."

6.3.5.3 Calibration Solution 3: Using a volumetric pipette, pipette **10.0mL** of the 2000ppm-perchlorate stock into a 50mL volumetric flask. Add **2mL** of 2M Ammonium Sulfate and fill to the mark with deionized or distilled water. Label as "*400ppm-perchlorate calibration standard*."

6.3.5.4 Calibration Solution 4: Add **2mL** of 2M Ammonium Sulfate into a 50mL volumetric flask. Fill to the mark with the *2000ppm-perchlorate stock* into to the mark. Label as "*2000ppm-perchlorate calibration standard*."

Final Concentration [ppm]	Volume of "2000 ppm Stock"	Volume of Distilled Water	Volume of 2M Ammonium Sulfate	Total Volume
20	0.5 ml	47.5 ml	2.0 ml	50 ml
200	5.0 ml	43.0 ml	2.0 ml	50 ml
400	10.0 ml	38.0 ml	2.0 ml	50 ml
2000	48.0 ml	0.0 ml	2.0 ml	50 ml

6.3.6 Calibration Curve analysis

6.3.6.1 Pour each 50 ml calibration stock solution into a separate, clean 100 ml beaker.

6.3.6.2 Starting with the lowest standard, immerse both electrodes into the beaker containing the calibration solution. Place a magnetic stirring bar in the solution. Stir the solution and allow the electrode reading to stabilize. Record the mV value on the *Analysis form*.

6.3.6.3 Plot the point on a graph of "mV" versus "ppm concentration".

6.3.6.4 Repeat after every 10 field samples.

6.3.7 Sample Analysis

6.3.7.1 Pipette **5mL** of sample solution from Step 6.2 into a 50mL volumetric flask.

6.3.7.2 Add **2mL** of **2M Ammonium Sulfate** solution.

6.3.7.3 Fill to the 50mL volume mark with deionized or distilled water and shake or swirl to mix.

6.3.7.4 Transfer to a 100mL beaker. Add a magnetic stir bar and immerse both electrodes. Spin the bar.

6.3.7.5 Allow the electrode reading to stabilize. Record the mV reading on the *Analysis form*.

6.3.7.6 Rinse the electrodes with deionized or distilled water between samples.

6.3.8 **Evaluation of Risk:** Evaluate the concentration of perchlorates in the field samples by comparison to the calibration solution.

- **Samples with a concentration of less than 500 ppm are considered negative for the risk of a fire or explosion hazard.**
- To quantify the perchlorate concentration: Divide the concentration in ppm by 4 to obtain the total weight of perchlorates in the sample in milligram. Divide the total weight of perchlorates by the surface area sampled to obtain the total weight per square foot. If the weight of perchlorates per square foot is less than 6.25 mg (equivalent to 500 ppm), then the sample is considered negative for the presence of perchlorates.

6.4 Clean-up

6.4.1 Dilute reagents and field sample solutions with tap water and discharge to sink. Flush the sink with water for 3 minutes.

6.4.2 Wash glassware with detergent. Rinse glassware thoroughly with tap water. Triple rinse with distilled or deionized water. Air Dry.

6.4.3 Thoroughly wipe up any spilled Perchloric acid on the counter top and equipment with a wet paper towel. Thoroughly rinse and wring out the paper towel in the sink three times. Dispose of the paper towel in trash. Flush the sink with water for 3 minutes.

7.0 References

7.1 Perchloric Acid Sampling and Analysis Procedure Manual, Oak Ridge National Laboratory, Oak Ridge, TN, 1993.

7.2 Orion Research Instruction Manual for the Perchlorate Ion Electrode, 1990.

8.0 Attachments

8.1 Analysis Form

8.2 Field Survey Form

BROOKHAVEN NATIONAL LABORATORY Safety & Health Services Division **INDUSTRIAL HYGIENE GROUP** Standard Operating Procedure	NUMBER **IH75200**
	REVISION **SHSD Final Rev 0**
SUBJECT: INSTRUMENT OPERATION: **Perchloric Acid Sampling and Analysis Procedure**	DATE **09-28-01**
	PAGE **10** OF 12

9.0 Documentation

Document Review Tracking Sheet		
PREPARED BY: *(Signature and date on file)* **A. Sells & R. Selvey** **Date 03/01/00**	**REVIEWED BY:** *(Signature and date on file)* **R. Selvey** **SHSD IH Group** **Date 09/27/01**	**APPROVED BY:** *(Signature and date on file)* **R. Selvey** **SHSD IH Group Leader** **Date 09/28/01**
Filing Code: **IH52QR.01**	**DQAR** **Date**	**Effective Date:** **09/28/01**

Periodic Review Record		
Date of Review	Reviewer Signature and Date	Comments Attached

BROOKHAVEN NATIONAL LABORATORY Safety & Health Services Division INDUSTRIAL HYGIENE GROUP Standard Operating Procedure	NUMBER IH75200 REVISION SHSD Final Rev 0
SUBJECT: INSTRUMENT OPERATION: Perchloric Acid Sampling and Analysis Procedure	DATE 09-28-01 PAGE 11 OF 12

Attachment 8.1: *Analysis Form*

Sample ID	Meter Reading (mV)	Perchlorate Concentration
Distilled Water (Pre-Test)		0
Ion Buffer (Pre-Test)		0
Calibration Standards		
Standard 20 ppm		20
Standard 200 ppm		200
Standard 400 ppm		400
Standard 2000 ppm		2000
Field Samples		
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
Distilled Water (Post Test)		0
Ion Buffer (Post-Test)		0

BROOKHAVEN NATIONAL LABORATORY Safety & Health Services Division INDUSTRIAL HYGIENE GROUP Standard Operating Procedure	NUMBER **IH75200** REVISION **SHSD Final Rev 0**
SUBJECT: INSTRUMENT OPERATION: **Perchloric Acid Sampling and Analysis Procedure**	DATE **09-28-01** PAGE **12** OF 12

Attachment 8.2 *Field Survey Form*

Date:	**Sample By:**

Building	**Room**	**Location**
Source/Operation Description:		
Suspected Sample Contents/Contaminant:		

Sample ID #	Specific Sample Location
1	
2	
3	
4	
5	